part of their own requirements. That had lowered the price in Canada and the United States very materially. Hydroquinone was being manufactured in the States and could now be obtained in any quantity. The cellulose acetate film was still being used, but was likely to be discarded in favour of another non-inflammable film. Eight tons of silver nitrate were used in Canada each year.

Mr. A. Nieghorn said that if a manufacture was carried on in Canada under German Patents when the terms of peace were arranged, the original manufacturer holding a patent would undoubtedly be allowed again to enter into competition with the manufacturer in a British Colony who had obtained a partial patent. That was only fair. That could be overcome by prohibiting the importation of the article or by protection. It was peculiar that in Canada the imports totalled nearly three hundred million dollars worth more than exports. The duty on chemicals, dyes, and medicines averaged under 6% of our total imports, while the general tariff for the two last fiscal years was something over 10½%. There seemed, therefore, room for some protection to be given to their young chemical industries. There were physical difficulties in the way of manufacturing some things. For instance, molybdenite was mined in Canada and dredged at tide-water in Florida. The Government could not protect them sufficiently to overcome that. There was room for the manufacture of several chemicals in a small way, but some assistance in the way of protection by the Government might be necessary.

Mr. Jas. Turner said that the reasons why England had not been prominent in the dye industry were due to non-support of the Government and of the capitalist. There was unlimited capital to be had for the dye industry to-day, and the Government had taken the matter up. In future England would be one of the largest producers of aniline dyestuffs and pharmaceutical products in the world. They had made α- and β-naphthol, H and G acids, and such things, but had not manufactured a great variety because the Germans had dumped their large surplus into England the same as sugar. Furthermore, in such things as nitrite of soda they could not compete, as the Germans made it by the lead process, and the English process was by sulphur. The litharge and other German by-products had made it impossible to compete. The plant where they were making β-naphthol, α-naphthol, H and G acids, and Clève acid ought in 6—12 months to be able to supply enough dyestuffs for England and the Colonies, but there were some products which could not be made on account of complicated patents. The duty on ethyl alcohol and methyl alcohol had been a hindrance to the colour industry for a long time, but when free alcohol had been obtainable they had put down one of the largest plants in the world for making dimethylaniline, Methyl Violet, Malachite Greens, etc. They could produce as much basic colours as any German manufacturer. If such a plant were started in Canada it would mean not only a plant for manufacturing dyes, but allied manufactures, such as a distillation plant for coal tar. The processes were elaborate and the consumption in Canada would not warrant any manufacturer putting down such a plant. But some things could be manufactured with profit: benzol and nitrobenzol for instance.

Mr. R. W. Breadner said that so far as he was aware, no bonuses were being granted in Germany on sugar, nor did the granting of bonuses ruin British refineries. In Canada raw sugar was not entitled to entry under the preferential tariff at the British preferential rate unless produced on British territory, and imported direct; and refined sugar was not entitled to the preferential rate unless it was made from raw sugar produced on British territory.

Mr. T. H. Wardleworth said that the history of the sugar question only went back about 100 years, as regards bounties. These had been instituted by Napoleon, and as a result the beet sugar manufacture was developed, bounties having been given until some ten years ago by Germany, Belgium, Russia, and France under convention. A few years ago that convention had broken up, and there was no bounty system to-day. Whatever the result of that may have been to the making of jams in England, to-day England commanded the markets of the entire world in confectionery, chocolate, and boiled sugars. From the refuse of the sugar beet was produced one of the finest carbonates of potash, 99·9%, and far more suitable than any other when a pure article was required; it might be made in Canada shortly. Canadian producers of silver could not produce metal good enough to make really good nitrate without a good deal of trouble. Some refineries left in it a trace of copper which necessitated re-working again and again. They also left bismuth and traces of other metals. What was wanted in Canada was to develop existing industries and resources, and it was better to ask not for protection in the way of duty so much as help from the Government in industrial research work. The Government should work through colleges and institutions. There seemed to be a want of co-ordination between the Government and educational institutions, and a want of co-ordination between the technical chemist and the manufacturer.

London Section.

Meeting held at Burlington House, on Monday, December 7th, 1914.

PROF. W. R. HODGKINSON IN THE CHAIR.

ON THE REDUCTION OF THE OXIDES OF ANTIMONY AND BISMUTH BY THEIR SULPHIDES.

BY W. R. SCHOELLER, PH.D.

Self-reduction, or the liberation of a metal by interaction of its oxide and sulphide with simultaneous evolution of sulphur dioxide, has been applied extensively in the metallurgy of lead and copper. All the available information concerning the behaviour of other metals under the same conditions appears to be confined to iron and antimony. Ferric oxide reacts with ferrous sulphide and produces ferroso-ferric oxide (this J., 1913, 1111); and since the two former are products of the action of heat and air on pyrites, their interaction provides a simple explanation of the presence of magnetic oxide of iron in copper mattes and roasted pyritic ores (this J., 1913, 738). Antimonious oxide and sulphide are invariably stated to fuse together without decomposition, forming "antimony-glass"; on the other hand, according to an isolated statement* which I have been unable to trace to its original source, a process based on the reaction between antimony tetroxide and sulphide is used "in some places" for the production of metal; while Schnabel† states that the tetroxide and sulphide when fused together yield antimony-glass. In a previous paper on the composition of liquated sulphide of antimony (this J., 1914, 169), I have shown that the latter contained a certain proportion of uncombined metal besides a considerable quantity of trioxide, from which it was inferred that self-reduction had taken place to a small extent while the material was in a fused condition.

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* Bloxam, Chemistry, Inorganic and Organic. 10th Edition, 476

† Schnabel-Louis, Handbook of Metallurgy, Vol. II., 433.

In view of these apparently conflicting statements, I have thought it desirable to ascertain whether the formation of antimony by the interaction of the sulphide and oxide is possible, and the experimental evidence given below proves this to be the case, but only under certain conditions which will be described later. The following facts have been established in the course of this research (the figures in brackets refer to the numbers of the experiments):

Antimony tetroxide containing one atom of "active" oxygen: $Sb_2O_4 = Sb_2O_3 + O$, reacts with the sulphide just below the fusion-point of the mixture: sulphur dioxide is given off in proportion to the quantity of tetroxide present, and the fused mass which results contains trioxide and sulphide (2 ; 4). It follows, then, that the course of subsequent self-reduction is independent of the nature of the oxide originally present. The following equations illustrate this point:—

$$\left\{\begin{array}{ll} Sb_2O_3 + 2Sb_2S_3 = 3Sb_2S_2O & (1) \\ 3Sb_2O_4 + 7Sb_2S_3 = 10Sb_2S_2O + SO_2 & (2) \end{array}\right.$$

$$\left\{\begin{array}{ll} 2Sb_2O_3 + Sb_2S_3 = 3Sb_2SO_2 & (3) \\ 3Sb_2O_4 + 2Sb_2S_3 = 5Sb_2SO_2 + SO_2 & (4) \end{array}\right.$$

In either case, the solubility of the resultant product in tartaric acid ($= Sb_2O_3$ content) is the same, whether the trioxide or tetroxide was used. The use of the above formulæ (Sb_2S_2O, oxysulphide; Sb_2SO_2, "sulphoxide") is not intended to imply that the corresponding compounds are formed in the fusion, as this is quite unlikely; but it is a convenient means of denoting the composition of the two mixtures.

Antimony trioxide and sulphide, fused together in a current of inert gas (*e.g.*, carbon dioxide), yield metallic antimony and sulphur dioxide: $2Sb_2O_3 + Sb_2S_3 = 6Sb + 3SO_2$ (or $Sb_2SO_2 = 2Sb + SO_2$). The reaction takes place in presence of an excess of either oxide or sulphide (10 ; 11). It begins soon after the fusion-point of the mixture has been passed (5) and becomes rapid at higher temperatures (8), but it is never complete on account of the volatilisation of both sulphide and oxide in the gas current; the highest yield of sulphur dioxide was 50% of the theoretical (9). The extent of the reaction increases with the relative surface of the fused mass exposed to the gas: if the latter be introduced into a Rose crucible, the fusion product contains but little metal (6 ; 14), whereas the use of a porcelain boat heated in a porcelain tube ensures a maximum yield (7—9). The foregoing remarks also apply to antimony-glass (14 ; 15). Metallic antimony is not formed if the oxide-sulphide mixture is fused in a crucible under a layer of salt (12 ; 13). A close analogy is thus established between the conditions affecting self-reduction and the volatility of the metal itself, for the metal volatilises at a bright-red heat in the air, or in a current of a gas, but not when fused under a layer of common salt.[*] Another example of the volatility of antimony compounds modifying the course of a reaction is quoted from Schnabel[†]: if antimony tetroxide be ignited with charcoal and alkali carbonates, metallic antimony is obtained; if the alkali be omitted, the greater part of the antimony will be volatilised as trioxide, a small part only being obtained in the metallic state.

The observations recorded above account for the formation of metallic antimony in certain metallurgical operations. First, if stibnite is roasted with insufficient access of air, some oxide will be formed and react with the unaltered sulphide, part of the antimony separating in the metallic state. This is demonstrated in Exp. 16, the two stages of which correspond to those of the Flintshire process of lead smelting, except that in the case of antimony a neutral gas current has to be maintained during the second stage. Secondly, as regards the liquation process, it is now established that self-reduction is the cause of the presence of reguline metal in crude antimony; no doubt the air charged with sulphur dioxide rising from the surface of the molten material plays the part of the gas current which is so important a factor in this reaction. It was ascertained that sulphur dioxide does not reduce antimonious oxide (17); it therefore takes no active part in the liberation of the metal. Thirdly, there is an obvious connection between self-reduction in a gas current and the converting of stibnite. Since writing my last paper I have discovered a previous reference[*] to the bessemerising of antimony sulphide; the article is merely a short statement to the effect that regulus of antimony may be obtained, together with sublimed sulphide, oxysulphide, or oxide, by blowing air through molten stibnite; no experimental data or details of practical working are added, and the abstract in the "Mineral Industry"[†]) conveys as much information as the original.

Bismuth. Nothing, apparently, has been published regarding the self-reduction of bismuth, which, having a more metallic character and a feebler affinity for oxygen than antimony, might be expected to react similarly to lead. My experiments prove that bismuth sulphide and oxide interact easily either in a current of carbon dioxide (18) or in a crucible under a layer of salt (20). The evolution of sulphur dioxide begins at a very low temperature, and the dark powder soon becomes a mass of tiny grey globules of metallic bismuth, which run together on increasing the heat. According to the equation: $2Bi_2O_3 + Bi_2S_3 = 6Bi + 3SO_2$, the yield of metal was 90% of the theoretical (20). The quantity of liberated metal was larger than that of evolved sulphur dioxide, and the non-metallic matter in which the buttons were embedded gave a distinct sulphate reaction, showing that a small proportion of basic bismuth sulphate was formed (19). This may be represented by the equation: $6Bi_2O_3 + Bi_2S_3 = 8Bi + 3(BiO)_2SO_4$. The formation of basic sulphate by oxidation of the sulphide and its stability at high temperatures are familiar facts in the metallurgy[‡] and analytical chemistry[§] of bismuth.

Experimental Part.

The experiments were carried out with pure antimony trioxide (Kahlbaum), tetroxide prepared from it by oxidation with nitric acid and subsequent ignition, and Japanese stibnite in large crystals. The latter is perhaps the purest form of antimony sulphide obtainable; the precipitated sulphide is almost invariably contaminated with chlorine. The mineral was ground to pass an 80-mesh sieve (I.M.M. standard); it assayed Sb 70·76%, insoluble 0·40%, As, *nil*, heavy metals less than 0·1%. Though crude antimony contains oxide and metal, it was used in experiments 13—15, together with a rich cervantite ore.

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[*] Roscoe and Schorlemmer, Treatise on Chemistry, 1907, Vol. II., 943.

[†] Schnabel-Louis, *loc. cit.*, 433.

[*] A. Germot, Revue des Produits Chimiques, 1907, **10**, 375.

[†] Mineral Industry during 1907, **16**, 53.

[‡] Schnabel-Louis, *loc. cit.*, Vol. II., 351.

[§] Low, Technical Methods of Ore Analysis, 5th Edition, 1911, 53.

Table I. shows the results of four experiments in which a porcelain boat containing mixtures of sulphide and trioxide or tetroxide was heated in a glass tube in a current of dry carbon dioxide; the escaping gas was passed through iodine solution to oxidise the sulphur dioxide, which was estimated in the usual manner. The contents of the boat were heated with a Bunsen burner until just fused, and left to cool under carbon dioxide. The fusion products were ground, and boiled with 5% tartaric acid solution for 30 minutes; the filtrates were made alkaline with bicarbonate and titrated with iodine: this gives the amount of Sb_2O_3 in the material. The sulphur evolved as dioxide is given in per cent. of the total quantity present in the stibnite. The molecular proportions correspond to equations 1—4 quoted above.

Table I.

Exp. No.	Molecular proportion.	S evolved as SO_2		Sb_2O_3 in fusion product.	
		Found.	Calculated.	Found.	Calculated.
1	$Sb_2O_4+2Sb_2S_3$	0·12%	0.	30·4%	30·0%
2	$3Sb_2O_4+7Sb_2S_3$	5·74%	4·76%	32·0%	
3	$2Sb_2O_3+Sb_2S_3$	0·05%	0	63·2%	63·1%
4	$3Sb_2O_4+2Sb_2S_3$	20·98%	16·67%	64·8%	

Exp. 5. The products obtained in the preceding experiments had the appearance and softness of stibnite. Nos. 3 and 4 were again fused in the same manner, but a higher temperature was maintained for 15 minutes, during which time sulphur dioxide was slowly evolved; the products after cooling were scoriaceous and iridescent, and showed a considerable increase in hardness. The tests were interrupted as the glass tubes bulged and broke.

Exp. 6. A glazed Rose crucible was now used so as to work at higher temperature in a current of carbon dioxide. 3·366 grms. Sb_2S_3 (2 mols.) and 4·566 grms. Sb_2O_4 (3 mols.) were fused with the full heat of a large Bunsen burner for 1 hour. The resultant product consisted of brown antimony-glass, in which was found a white metallic globule of crystalline fracture, weighing 0·0258 grm. and assaying 98·9% Sb. (Compare Exp. 11.)

In the experiments summarised in Table II. a porcelain tube containing the porcelain boat was heated in a short combustion furnace. Arrangements for passing dry carbon dioxide and absorbing the sulphur dioxide were the same as in Exp. 1—4. The direct determination of the metallic antimony formed in these tests being impossible, the amount of sulphur dioxide evolved was taken as the measure of the degree of self-reduction.

Table II.

Exp. No.	Molecular proportion.	S evolved as SO_2 = Degree of self-reduction.
7	$2Sb_2O_3+Sb_2S_3$	21·0%
8	$2Sb_2O_3+Sb_2S_3$	41·6%
9	$2Sb_2O_3+Sb_2S_3$	49·7%

Exp. 7 was interrupted before the reaction was complete, as a fairly large quantity of mixture was taken in order to obtain enough pure metal for an antimony determination: the SO_2-figure is therefore low. The metallic buttons were detached from the boat, and cleaned from adhering sulphide, etc.; they assayed 97·8% Sb.

In Exp. 8 a thermo-couple was introduced. The temperature was slowly raised, and after 40 minutes remained constant at 965° C., where it was kept for half an hour, so as to secure a maximum yield of sulphur dioxide: 41·6% was obtained. The boat was practically empty, except for a film of yellow glass; the sublimate in the cold part of the tube consisted of white metallic globules and a steel-grey crust of sulphide and oxide.

Exp. 9. In the preceding test a 4-in. boat was heated in a 6-in. sectional furnace. Another 6-in. section was now placed behind that containing the boat, but this addition to the heated area did not greatly increase the extent of self-reduction: 49·7% of the total sulphur was evolved as dioxide. Sublimate and residue were the same as in the last experiment.

Exp. 10 and 11. Two mixtures, the first containing an excess of oxide ($5Sb_2O_3+Sb_2S_3$), the other an excess of sulphide ($5Sb_2S_3+Sb_2O_3$), were treated as before in the porcelain tube. In both cases much sulphur dioxide was given off, and globules of regulus formed. By-products were obtained as follows: with excess oxide, a slight residue of orange-red antimony-glass and a sublimate containing white needles of antimonious oxide; with excess sulphide, a residue and globular sublimate of sulphide, easily distinguishable from the metal itself.

Exp. 12. A covered crucible, containing a mixture of sulphide and oxide ($Sb_2S_3+2Sb_2O_3$) under a layer of salt, was heated in a muffle for 45 minutes. The fusion product consisted of red antimony-glass which, except for a slight silicious residue, was completely soluble in hot hydrochloric acid: no regulus could be detected. (See also Exp. 13.)

In the three following experiments, which demonstrate the formation of metal from antimony-glass, crude antimony and an oxidised ore were used. The presence of free metal in the crude did not interfere, as the tetroxide of the cervantite oxidises the antimony, thus: $3Sb_2O_4+2Sb=4Sb_2O_3$. (Schnabel, p. 433.)

Exp. 13. Two covered crucibles containing the same charge, viz., equal parts of powdered crude and cervantite ore, were heated for 1 hour to about 1000° C. in a muffle; a layer of salt was used in one crucible, borax-glass in the other. In both cases reddish-brown glass was obtained, which was found to be free from metallic antimony.

Exp. 14. The glass obtained in the preceding experiment was fused under carbon dioxide in a Rose crucible for 1 hour, using a Teclu burner. No button was found as in Exp. 6, but on digesting the powdered glass with hot hydrochloric acid, a small quantity of regulus was detected by its characteristic colour and lustre. It may be stated here that antimony sulphide and the metal can be "parted" with hydrochloric acid, and that the latter cannot be mistaken for the former; the separation is not quantitative, as an appreciable amount of regulus dissolves. (This J., 1913, 260. Solubility of Sb in Sb_2S_3: this J., 1906, 376.)

Exp. 15. The same glass was again fused in a current of carbon dioxide, this time in the porcelain tube. After 30 minutes' heating, the boat presented a striking appearance: it was full of large, white, metallic beads.

Exp. 16 illustrates the formation of metal from stibnite. The mineral was fused at a gentle heat in a current of air, which converted it into a mixture of sulphide and trioxide, part of the latter escaping as fume. The air was then replaced by a current of carbon dioxide, and the temperature raised to about 950° C. The fusion product contained a considerable proportion of metallic antimony, which was detected by "parting" with hydrochloric acid.

Exp. 17. Antimonious oxide was fused for some time in a current of sulphur dioxide, and the escaping gas passed through barium chloride solution. No decomposition of the oxide was observed, nor was any barium sulphate obtained in the receiver.

Bismuth. The oxide was prepared by ignition of pure bismuth nitrate, and the sulphide by precipitation of the same salt with sodium sulphide. The results of the experiments are shown in Table III.

TABLE III.

Exp. No.	Molecular proportion $2Bi_2O_3+Bi_2S_3$.	Metallic Bi.	SO_2 evolved.
18	Glass tube ; CO_2 current	not determined	63·1%
19	Porcelain tube ; CO_2 current	78·4%*	68·1%
20	Crucible ; salt-cover	87·8%*	not determined

* Not quite quantitative : see below.

Exp. 18 was made in the apparatus described under antimony. Table I. At a very low temperature the mass darkened and gave off sulphur dioxide without showing any sign of fusion. The experiment was stopped after 10 minutes as the tube commenced to soften ; the product after cooling consisted of minute metallic globules cemented together, which disintegrated on digestion with moderately strong hydrochloric acid : this solution was found to contain sulphate.

Exp. 19 corresponds to the high-temperature experiments with antimony. Table II. The porcelain tube was heated for 30 minutes to about 950° C. The porcelain boat was found to contain several large and small buttons of bismuth which were collected and weighed : slight losses occurred in detaching them. A colourless residue, giving sulphate reaction, coated part of the boat.

Exp. 20. A covered glazed Rose crucible containing the oxide-sulphide mixture under a deep layer of salt was heated for 15 minutes over a Teclu burner. Minute globules of metal round the inner edge of the crucible gave evidence of volatilisation, in spite of which the amount of bismuth collected and weighed was 87·8% of the theoretical.

My thanks are due to Messrs. G. T. Holloway and Co., Ltd., for facilities afforded in the experimental work and their permission to publish the results.

In reply to a question, the author said he had not carried out the reactions on any larger scale than a purely laboratory one.

THE REMOVAL OF CARBON BISULPHIDE FROM COAL GAS.

BY E. V. EVANS, F.I.C.

The numerous chemical and physical processes that have from time to time been proposed for the removal of carbon bisulphide from coal gas are briefly described by Witzeck (J. Gasbeleucht., 1903, 21 *et seq.*), whilst the history of the subject, with special reference to processes involving the heating of gas, has been compiled by Dr. Charles Carpenter, and is included in his lecture delivered recently to the Institution of Gas Engineers at Liverpool (see this J., 1914, 737).

The sulphur compounds remaining in coal gas after the extraction of sulphuretted hydrogen consist mainly of carbon bisulphide, and the proportion by volume of this constituent in the gas represents only about 0·02%. Considering the immense volumes of gas to be dealt with in the case of a modern London Gas Works it is obvious that the elimination of this impurity, owing to its state of extreme dilution, should be effected by a chemical reaction of high velocity. The initial stages of a laboratory investigation were therefore directed towards ascertaining the relative intensities of known reactions of carbon bisulphide, provided such reactions entailed the use of reagents suitable for application on the large scale. These may be collectively described under three headings :—

(1) The extraction of carbon bisulphide by alkalis or alkaline earths, in the presence of sulphuretted hydrogen.

(2) The interaction of carbon bisulphide and certain amino compounds, such as aniline, either with or without the use of catalytic agents.

(3) The decomposition of carbon bisulphide by heat, with or without the presence of catalysts.

The "Athion" process which utilizes alkaline cellulose for the extraction of carbon bisulphide from gas previously freed from carbon dioxide is of recent origin and was not examined by the author.

1. *Alkalis and alkaline earths.*—The purification of gas by lime is based on the absorption of carbon bisulphide by an active sulphided compound, with the formation of a thiocarbonate. As thiocarbonates are readily decomposed by carbon dioxide, the extraction of this constituent of the gas is essential. Carbon dioxide, though inevitably produced in the manufacture of gas, is not an impurity, and the necessity of removing it is an impediment to the economic efficiency of any process. When lime is employed to remove carbon dioxide, the cost of raw material alone represents about ¼d. per 1000 cubic feet of gas purified, which is more than the total working costs of a process to be described later. It has been stated by Sabatier and others that the major portion of carbon dioxide may be extracted by washing the gas with solutions of potassium carbonate, the resulting bicarbonate being decomposed by heat with regeneration of the carbonate. This reaction is a slow one, and its application on a large scale necessitates the employment of extensive apparatus. It has, further, been proposed to recover, for sale, the carbon dioxide evolved in the regeneration process, but this obviously cannot receive wide application, as the output of a few large works would crush the market.

The nature of the reactions involved in the lime process of gas purification has been demonstrated by Divers and Veley (see this J., 1884, 481, 550 ; 1885, 633), and the work of these investigators was repeated in the laboratory. Slaked lime yields, by the action of gas containing sulphuretted hydrogen, a sulphided compound capable of arresting carbon bisulphide with the formation of a basic calcium thiocarbonate. The intermediate and final products of this reaction were prepared, and all laboratory operations demonstrated the extreme sensitiveness of the reaction to outside influences. A portion of the intermediate sulphided compound—considered by Divers to be calcium hydroxyhydrosulphide—became oxidised and rendered inactive by oxygen contained in small quantity in the gas, whilst the final product, the basic thiocarbonate, was not only decomposed by carbon dioxide, but was dissociated at slightly increased temperatures. Taking advantage of this instability to the influence of heat, an unsuccessful attempt was made to place the lime process on a more practical basis, by rendering possible the regeneration of spent material *in situ*, and thus to overcome the nuisance associated with spent lime. This scheme proved satisfactory only when utilising pure reagents, and failed completely when applied to the coal gas mixture, owing to the oxidation of active sulphides to sulphites and thiosulphates, which preclude regeneration, and to the difficulty of determining the conditions most favourable to the extraction of carbon bisulphide; and at